PATENT COOPERATION TREATY

PCT

INTERNATIONAL-TYPE SEARCH REPORT

(PCT Article 15.5)

National application No.	Country or Office of filing	Applicant's or agent's file reference
19981490	FI	

Filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
29 June 1998	

Applicant

Kemira Agro Oy

Date of request for international-type search	International-type search request No.
20 July 1998	FI 98/00001

This international-type search report has been prepared by this International Searching Authority and is transmitted to the applicant.

This international-type search report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (See Box I).

2. [ ] **Unity of invention is lacking** (See Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international-type search was carried out on the basis of the sequence listing

   [ ] filed with the international application.

   [ ] furnished by the applicant separately from the international application,

      [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.

   [ ] transcribed by this Authority.

INTERNATIONAL-TYPE SEARCH REPORT

Search request No.
FI 98/00001

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C05G 5/00, C05B 19/00, C05C 3/00, C05C 9/00, C05D 1/02, B01J 2/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C05B, C05C, C05D, C05G, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL, EDOC, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9629287 A1 (DEAD SEA WORKS LTD.), 26 September 1996 (26.09.96), page 2, line 11 - page 3, line 12; page 6, line 1 - page 8, line 18, figures 1,2 --	1-9
A	GB 1159445 B (PRODUITS CHIMIQUES PECHINEY-SAINT-GOBAIN), 23 July 1969 (23.07.69), page 1, line 43 - page 2, line 34, claims 1-9,14, 15 --	1-9
A	US 4008064 A (ÖYVIND SKAULI), 15 February 1977 (15.02.77), column 1, line 1 - line 12; column 2, line 13 - column 3, line 35; column 4, line 27 - line 44, column 6, line 19 - line 47; figure 1; claims 1,4-6; abstract --	1-9

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international-type search	Date of mailing of the international-tupe search report
16 December 1998	1998 -12- 18
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Ingrid Grundfelt Telephone No. +46 8 782 25 00

INTERNATIONAL-TYPE SEARCH REPORT

Search request No.
FI 98/00001

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WPI/Derwent´s abstract, Accession Number 80-19312, week 8011, ABSTRACT OF JP, 55015655 (HITACHI METALS LTD), 02 February 1980 (02.02.80); & Patent abstracts of Japan, JP 55015655, vol.04, no. 42, 03 April 1980 (03.04.80)	1-9

--

INTERNATIONAL-TYPE SEARCH REPORT
Information on patent family members

01/12/98

Search request No.
FI 98/00001

WO	9629287	A1	26/09/96	AU	5146696	A	08/10/96
				CA	2213738	A	26/09/96
				IL	113104	D	00/00/00
GB	1159445	B	23/07/69	BE	699808	A	12/12/67
				DE	1592734	A	10/02/72
				DK	130632	B,C	17/03/75
				ES	341700	A	01/07/68
				NL	6708178	A	14/12/67
US	4008064	A	15/02/77	AU	8335975	A	27/01/77
				BE	831779	A	17/11/75
				BG	39806	A	15/08/86
				BR	7504741	A	06/07/76
				CA	1063778	A	09/10/79
				DD	118995	A	05/04/76
				DE	2533328	A,C	12/02/76
				DK	137068	B,C	16/01/78
				DK	338275	A	27/01/76
				EG	11720	A	29/03/78
				FI	62628	B,C	29/10/82
				FI	752127	A	27/01/76
				FR	2279457	A,B	20/02/76
				GB	1490003	A	26/10/77
				IE	41302	B	05/12/79
				IN	142375	A	02/07/77
				JP	1115790	C	29/09/82
				JP	51037098	A	29/03/76
				JP	56048202	B	14/11/81
				KE	2852	A	04/08/78
				NL	184097	B,C	16/11/88
				NL	7508914	A	28/01/76
				OA	5060	A	31/12/80
				SE	395617	B,C	22/08/77
				SE	7508183	A	28/01/76

15

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
47497/JS/BK		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/FI99/00568	28/06/1999	29/06/1998
International Patent Classification (IPC) or national classification and IPC C05G5/00		
Applicant KEMIRA AGRO OY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
24/12/1999	12.09.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Grundke, H Telephone No. +49 89 2399 8564

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/FI99/00568

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-18	as published				

Claims, No.:

9-18	as published				
1-8	as received on	12/07/2000	with letter of	07/07/2000	

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-18
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Item V:

Reference is made to the following document/s/:

D1: US-A-4 008 064
D2: GB-A-1 462 633

The claimed process route departs over art recognized routes of granulation as set out e.g. in documents D1 or D2 by feeding the feed material or a part thereof into a melter for melting a desired portion thereof and feeding only partly molten material to the granulator. This route produces unexpectedly high quality products having superior physical properties (granule strength, abrasion, dusting) compared to commercial products.

Item VIII:

Since the claims have been changed the description will need amendment for conformity therewith.

Claims

1. A process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of:
providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material,
feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state,
feeding the ~~molten or~~ partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and
cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution,
provided that no water or aqueous liquid is introduced into the process.

2. A process according to claim 1, wherein the process is carried out continuously, and the molten portion of the feed material is kept constant during the process by controlling the flow rate of the feed material and the temperature of the melter.

3. A process according to claim 1 or 2, wherein the temperature of the ~~molten or~~ partly molten feed material is between 70 °C and 135 °C.

4. A process according to any of claims 1-3, wherein the melting is effected by introducing hot air into said melter.

5. A process according to claim 4, wherein the temperature of the hot air introduced into the melter is between 200 °C and 550 °C.

6. A process according to any of claims 1-5, wherein from 10 to 40% by weight of the feed material melts in the melter.

7. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises all individual components of the raw materials.

8. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises one or some of the individual components of the raw materials, and the rest of the components is fed to the granulator.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
47497/JS/BK		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/FI99/00568	28/06/1999	29/06/1998
International Patent Classification (IPC) or national classification and IPC C05G5/00		
Applicant KEMIRA AGRO OY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
24/12/1999	12.09.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Grundke, H Telephone No. +49 89 2399 8564

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/FI99/00568

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-18	as published				

Claims, No.:

9-18	as published				
1-8	as received on	12/07/2000	with letter of	07/07/2000	

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-18
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-18
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-18
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Item V:

Reference is made to the following document/s/:

D1: US-A-4 008 064
D2: GB-A-1 462 633

The claimed process route departs over art recognized routes of granulation as set out e.g. in documents D1 or D2 by feeding the feed material or a part thereof into a melter for melting a desired portion thereof and feeding only partly molten material to the granulator. This route produces unexpectedly high quality products having superior physical properties (granule strength, abrasion, dusting) compared to commercial products.

Item VIII:

Since the claims have been changed the description will need amendment for conformity therewith.

W/V

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C05G 5/00, C05B 19/00, C05C 3/00, 9/00, C05D 1/02, B01J 2/00

A1

(11) International Publication Number: **WO 00/00452**

(43) International Publication Date: 6 January 2000 (06.01.00)

(21) International Application Number: PCT/FI99/00568

(22) International Filing Date: 28 June 1999 (28.06.99)

(30) Priority Data:

981490	29 June 1998 (29.06.98)	FI
982013	18 September 1998 (18.09.98)	FI

(71) Applicant *(for all designated States except US)*: KEMIRA AGRO OY [FI/FI]; Porkkalankatu 3, FIN–00180 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: VAN BREMPT, Arthur [BE/BE]; Daalstraat 111, B–1852 Grimborgen (BE). POUKARI, Juhani [FI/FI]; Tinankuja 4 D 24, FIN–12430 Masala (FI).

(74) Agent: BERGGREN OY AB; P.O. Box 16, FIN–00101 Helsinki (FI).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: A PROCESS FOR THE PREPARATION OF COMPOUND FERTILIZER GRANULES

(57) Abstract

The invention relates to a process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of: providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material, feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state, feeding the molten or partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution, provided that no water or aqueous liquid is introduced into the process.

2

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

A process for the preparation of compound fertilizer granules

The present invention relates to a process for the preparation of compound fertilizer granules by using solid granulation.

The term "compound fertilizer" is defined and used with several different meanings; it contains at least two of the plant nutrients nitrogen, phosphorus, and potassium. Compound fertilizers are produced chemically or by blending. They shall be in the form of granules, pellets, prills, or crystals and shall be free-flowing.

Compound fertilizers are manufactured and frequently used because they are convenient to produce, transport, store and apply and because they fulfil local or regional nutrient requirements, especially basal nutrient needs well. In addition to containing various ratios of the primary nutrients ($N + P_2O_5 + K_2$), the compound fertilizers may contain certain secondary and micronutrients specific to the crop needs in particular agroclimatic regions.

Granulated fertilizers have several advantages over powders, particularly in decreasing the quantity of dust, improving uniformity of flow when fertilizers are applied and segregation when they are blended.

In classifying the granulation methods, the physical properties of the materials to be granulated will be used. According to the density of the materials the following three groups may be distinguished: granulation of solids, granulation of slurries or of melts and granulation of fluids simultaneously with the reaction by which the product is formed.

Basic processes for manufacturing compound fertilizers are: Steam/water granulation, Chemical granulation or complex or slurry granulation, Drop forming or prilling, Compaction granulation and Dry mixing or blending.

The principal mechanisms responsible for initial fertilizer granule formation and subsequent growth are agglomeration and accretion. The known and widely applied compound fertilizer granulation methods are well reported for example in "Fertilizer Manual", Kluwer Academic Publishers, 1998, p. 434-451 and "Studies of Granulation of Compound Fertilizers Containing Urea: A Literature Review", G.C. Hicks, National Fertilizer Development Center; Bull Y-108, 15 pp., 1976.

Accretion is a process in which layer upon layer of a fluid material is applied to a solid particle causing it to grow in size; for example slurry-type granulation processes used to produce DAP, MAP, TSP, and some nitrophosphate compounds are accretion-type of granulation processes.

Agglomeration or granulation of solid particles is a classical method to granulate fertilizers, for example NPK products. In most agglomeration-type NPK formulations, 50-75% of the raw materials are fed as solid particles. The (premixed) raw materials are fed to a granulator where agglomeration is initiated. In the granulator steam and/or water or other liquid is added to provide sufficient liquid to enhance granulation. In same processes a small amount ammonia may also be added to promote granulation and improve product quality by increasing the CHR (critical relative humidity) and decreasing the acidity. The solid particles are assembled and joint into granules by a combination of mechanical interlocking and cementing.

A number of industrial scale processes to manufacture compound fertilizers are developed and applied. In the steam/water granulation process steam and/or water or scubber liquid is added into the granulator to provide sufficient liquid phase and plasticity to cause the dry raw materials to agglomerate into the product-size granules required.

The use of urea as a N-source for fertilizers of the different types and grades has established. Solid urea with quite high biuret content (0,8-2,0 wt-%) is mainly used for direct application to the soil and weak aqueous urea solutions with low biuret (max 0,3 wt-%) are used as foliage sprays.

The use of urea has also established in the manufacture of (granular) compound fertilizers based on for example superphosphate or ammonium phosphate.

The conventional wet granulation is not a suitable method for producing formulations containing urea, particularly when potassium chloride is also present, because the product is very hygroscopic and therefore difficult and expensive to dry.

In the chemical granulation beside a great amount of solid raw materials, water, steam, scrubber liquid, and/or ammonia and acid are fed to the granulator; the granules are formed mostly by agglomeration but in some processes granule formation may occur by accretion, too.

Drop formation or prilling, compaction granulation, dry mixing or blending, etc. are also applied quite widely to produce different granular fertilizer formulations.

Because some water or moisture is always present in most traditional granulation processes, drying is an obligatory, difficult and expensive stage of the processes and cause the need of a separate dryer construction. To solve problems of granulation, product quality and drying different fertilizer grade-dependent processes are development.

A granulation process is described by Doshi, S.R. in the article "Fusion blend", Fertilizer Research vol. 30(1): p.87-97, 1991. Water (or steam) has been used to agglomerate solids either in powder, prilled or granulated form but no other liquids such as ammonia, phosphoric acid, or nitric acid are involved in the described process; still drying is essential.

Some water or moisture is always included in the process. The process is temperature and material moisture-related. For example, for the most agglomeration-type NPK fertilizers a liquid phase of about 300 kg/t of product is shown to be optimal.

Patent publication GB 1,189,398 (Sumitomo) discloses a process for producing a NK fertilizer which process comprises spraying a liquid mixture of urea, potassium chloride, gypsum and 1-10% by weight of water onto the solid material in a granulator. No drying is used. However, the amount of water added into the process is high enough to keep urea in dissolved state and the final product has a quite great water content of 1-2% by weight.

Patent publication US 4,138,750 (TVA) discloses a process for the production of fertilizers from phosphoric acid, sulfuric acid, anhydrous ammonia and urea where a specially designed pipe-cross reactor is used to produce a homogenous melt or slurry of low moisture content from phosphoric acid, sulfuric acid and anhydrous ammonia. The pipe-cross reactor eliminates the need for a preneutralizer and in addition, because of the low melt or slurry moisture content, the dryer is eliminated. The neutralization reaction heat is drying the material in the pipe-cross reactor.

Because of the water/moisture content of the raw materials and products, process and product quality problems, like increased hygroscopicity and plasticity, will often occur when fertilizers are granulated by using steam/water and chemical granulation processes; particularly when, for example SSP, TSP and/or urea is present in the product. The hygroscopicity and plasticity complicate drying,

screening and crushing operations, and furthermore, the storage properties of those compound fertilizers are often inferior to those of fertilizers that do not contain these substances.

The present invention is developed to solve the granulation, product quality, and storage etc. problems in manufacturing of compound fertilizers. The present invention relates to a process for the preparation of compound fertilizers such as NPK, NK etc., where solid raw materials are mixed in a mixer and fed to a granulator, whereto hot air is also fed. The raw materials are granulated without the aid of water or any other liquid such as ammonia, phosphoric acid or sulfuric acid. Thus, the granulation is a true solid granulation process. Because water or any other liquid is not added, there is no need for drying the granulated product. Further more the physical quality of the product is good, too.

Particularly, the process of the present invention has great advantages to the known granulation methods which require higher temperatures at the drying phase. Particularly, controlling of the humidity and drying temperature is important and difficult; the high temperature may cause melting of the granulated material and it will stick to the interior walls and flights of the dryer near the discharge end. The optimal values for humidity and temperature vary greatly from product to product.

Thus, the present invention provides a process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of:
providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material,
feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state,
feeding the molten or partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and
cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution,
provided that no water or aqueous liquid is introduced into the process.

The melting of the feed material or a part thereof in the melter can be effected by introducing hot air into the melter. The melting can also be effected by other means, for example by heaters.

According to a preferred embodiment of the invention the process is carried out continuously, and the molten portion of the feed material is kept constant during the process by controlling the flow rate of the feed material and the temperature of the hot air introduced into the melter. The optimal proportion of the molten feed material is dependent on the grade of the fertilizer wanted and the raw materials used. The optimal proportion of the molten material can for example be about 10-40 wt-%, preferably about 10-25 wt-%, more preferably about 12-20 wt-%, depending on the grade.

When melting is carried out by the aid of hot air a suitable temperature of the hot air introduced into the melter is between 200 and 550 °C. At the melter outlet the hot air has a temperature of about 90 °C to 120 °C.

Suitably the temperature of the molten or partly molten feed material leaving the melter is between 70 °C and 135 °C, preferably between 70 °C and 110 °C.

The process of the invention can be carried out either by introducing all individual components of the raw materials into the melter or by introducing one or some of the individual components of the raw materials into the melter and the rest of the components into the granulator.

The material to be fed into the melter and/or granulator can be preheated. This is preferred in view of the temperatur control of the process. The material can suitably be preheated to a temperature in the range from about 80 °C to about 110 °C.

The granulation temperature can vary depending on the formula of the fertilizer. The granulation temperature is preferably between about 75 °C and about 125 °C, more preferably between about 80 °C and about 125 °C.

The temperature of the cooled granulated product to be screened is typically between about 40 °C and 60 °C.

Typical solid fertilizer raw materials which can be used in the present invention are e.g. urea, diammonium phosphate (DAP), K_2SO_4 (SOP), monoammonium phosphate (MAP), phosphate rock, potassium chloride (MOP i.e. KCl), single superphosphate (SSP), triple superphosphate (TSP), ammonium sulfate (AS) and ammonium chloride (AC).

Preferably the fertilizer raw materials comprise urea, especially urea prills, and at least one other fertilizer raw material.

Additionally magnesium sulfate and/or one or several trace elements i.e. micro-nutrients, such as boron, can be added.

Furthermore bentonite, calcite, calcium oxide, calcium sulfate (anhydrous or hemihydrate), dolomite and/or sand and/or any other conventionally used filler can be added.

According to the present invention all solid raw materials (solid fertilizer raw materials and optionally recycle material, micro nutrients and fillers) can be introduced into the melter. However, it is also possible to introduce a part of the solid raw materials into the melter and the remaining solid raw materials into the granulator.

In a preferred embodiment the process of the invention comprise the step of screening the granulated product to obtain dry compound fertilizer granules having a size of 2 to 5 mm.

The undersize material (< 2 mm) and the oversize material (> 5 mm) obtained in the screening can be recirculated as said recycle material. Optionally the oversize material can be milled after the screening before being recirculated. The temperature of the recycle material from the screening is typically about 60 °C or less.

The melter and granulator can be separate units but the melter and granulator can also be part of the same equipment.

This invention has advantages over the traditional granulation methods of the prior art technology because the raw materials are granulated without the aid of any water or any other liquid such as ammonia, phosphoric acid or sulfuric acid. Because water or any other liquid is not added, there is no need for drying of the product. This makes the granulation operation more simple and investment costs less expensive because no separate equipment for drying is needed.

The final product will have a low water content (0.2-0.6 wt-%) originating from the raw materials. No supplementary drying is required. The water content of the products produced by traditional methods is normally about 1-2 wt-% causing already mentioned caking and applying problems.

The invention is illustrated in and by the following examples. Additionally the strenght of the product granules obtained in the following examples was checked after a 3 months' storage, and the strenght was found to be unchanged.

Example 1

Bench scale process for solid granulation.

Formulas (kg/t)

	GRADE		
Raw material	15-15-15 DAP+SSP	15-15-15 MAP+Sand	17-17-17 MAP+NH_4Cl
Urea	249	255	204
MAP(Lithuania 11-50)	-	300	340
DAP(Pernis 17-45)	210	-	-
SSP(Lithuania 19%)	287	-	-
NH_4Cl (N 26%)	-		153
KCl (K_2O 60%)	250	250	284
Sand	-	175	-

The mixture of the solid raw materials was fed to the bench scale granulator. Urea was added as prills. The melting of the mixture happened with hot air at the beginning of the granulator. Granulation was carried out at the granulator and partly at the cooler.

The process conditions and results are shown in Table 1.

Table 1

	GRADE		
	15-15-15 DAP+SSP	15-15-15 MAP+Sand	17-17-17 MAP+NH_4Cl
Process conditions:			
Feed + recycle kg/h	8.3	10.1	11.9
Recycle ratio	0.2	0.2	0.2
Air heater			
- temperature °C	336	316	322
- pressure bar	1.8	1.8	1.8
Temperature of product			
granulator outlet °C	97	92	97
cooler outlet	30	32	35
Granulation	Good	Very good	Good

Product properties:

H_2O (KF)	%	0.25	0.15	0.28
N	%	15.2	16.1	18.2
P_2O_5 total	%	15.9	15.0	17.1
K_2O	%	15.8	16.7	18.5
Granule strength N		52	40	50
Abrasion %		0	0.2	0.7
Shattering %		37	32	45
CRH %		34	35	43
Moisture absorption 80% RH				
2 h	%	2.8	2.7	3.2
4 h	%	5.7	5.5	6.2
6 h	%	8.8	8.3	9.1

The grade 15-15-15 granulated better when it contained MAP + sand than DAP + SSP.

The grade 17-17-17 containing ammonium chloride granulated good, too. Ammonium chloride reacted partly with urea and formed urea · NH_4Cl. Nutrient content of each product was good. Physical properties of the products were good; he products were very dry.

Example 2

Bench scale process for solid granulation

GRADE	**NK 16-0-31**	
	2A	2B
Formula	16-0-31 Filler bentonite kg/t	16-0-31 Filler $CaSO_4$ hemihydrate kg/t
Urea (prills)	348	348
KCl (white)	517	517
Bentonite	125	-
$CaSO_4*0.5H_2O$ (as dry matter)	-	125

The mixture of solid raw materials was fed with the recycle to the bench scale granulator. Melting happened with hot air at the beginning of the granulator. Granulation has been carried out at the granulator and partly at the cooler.

The products were coated with Esso coating oil 2 kg/t + talc 3 kg/t.

Very good or good granulation was obtained with a good product quality. However, the great humidity of air during the process caused some immediate increase of the water content of the final product.

The process conditions and results of the product tests are shown in Table 2.

Table 2

GRADE		**NK 16-0-31**	
		2A	2B
		16-0-31	16-0-31
		Filler	Filler $CaSO_4$
		bentonite	hemihydrate
Feed + recycle kg/h		9.0	9.0
Recycle ratio		0.7	0.4
Air heater			
- temperature	°C	294	238
- pressure	bar	1.6	1.6
Temperature of fert	°C		
- granulator outlet		104	88
- cooler outlet		28	27
Granulation		Very good	Good
Product properties			
Chemical analyses			
Water (KF)	%	0.77	0.78
Urea - N	%	16.6	16.8
N	%	16.6	16.8
K2O	%	31.8	30.9
S	%	0.51	3.0
pH		7.3	5.6
Physical properties			
Granule strenght	N	27	41
Abrasion	%	1.3	1.1
Volume weight	kg/l	0.77	0.80
Flowability	kg/min	4.83	4.80
Shattering	%	52	45
CRH	%	40	38
Moisture absorption			
80% RH			
2 h	%	2.9	2.7
4 h	%	5.0	4.5
6 h	%	7.0	6.8

Example 3

Bench scale process for solid granulation

GRADE	**18-12-6+1.5MgO**
	kg/t
Urea (prills)	172
KCl (white)	100
Kovdor phosphate	155
DAP (Pernis) 17-45	143
AS (Leuna)	366
$MgSO_4$	53

The mixture of solid raw materials was fed with the recycle to the bench scale granulator. Melting happened with hot air at the beginning of the granulator. Granulation has been carried out at the granulator and partly at the cooler.

The products were coated with Esso coating oil 2 kg/t + talc 3 kg/t.

Very good granulation was obtained with a good product quality. The process conditions and results of product tests are shown in Table 3.

Table 3

GRADE		**18-12-6+1.5MgO**	
Feed + recycle kg/h		9.0	
Recycle ratio		0.6	
Air heater			
- temperature	°C	233	
- pressure	bar	1.6	
Temperature of fert °C			
- granulator outlet		98	
- cooler outlet		28	
Granulation		Good	
Product properties			
Chemical analyses			
Water (KF)	%	0.36	
Urea - N	%	8.5	
NH_4 - N	%	9.7	
N	%	18.2	
P_2O_5 - Total	%	11.3	
P_2O_5 - NAC	%	6.0	(53%)
P_2O_5 - WS	%	5.5	(49%)
K_2O	%	8.4	
Mg	%	1.3	
S	%	10.8	
pH		5.8	
Physical properties			
Granule strenght	N	41	
Abrasion	%	0.6	
Volume weight	kg/l	0.84	
Flowability	kg/min	4.88	
Shattering	%	59	
CRH	%	40	
Moisture absorption			
80% RH			
2 h	%	3.3	
4 h	%	5.2	
6 h			

Example 4

Bench scale process for solid granulation

GRADE	**12-12-17+2 MgO + 0.5 B_2O_3**
	kg/t
Urea (crushed)	264
Morocco phosphate	270
TSP (P_2O_5 45%)	89
KCl (white)	284
$MgSO_4$	64
Colemanite	6

The mixture of solid raw materials and recycle was preheated to about 100 °C in the feeding screw of the granulator. Melting happened with hot air at the granulation drum. Granulation has been carried out at the granulator and partly at the cooling drum.

The products were coated with SK Fert FW5 AG 2 kg/t + talc 3 kg/t.

Very good or good granulation was obtained with a good product quality. The process conditions and results of product tests are shown in Table 4.

Table 4

	GRADE		**12-12-17+2 MgO + 0.5MgO**	
	Feed + recycle kg/h		5.3	
	Recycle ratio		0.6	
	Granulation temperature °C		About 120	
	Air from cooler	"	27	
	Granulation		Good	
	Product properties			
	Chemical analyses			
	Water (Kf)	%	0.35	
	Urea - N	%	12.4	
	P_2O_5 - Total	%	12.2	
	P_2O_5 - NAC	%	6.0	(49%)
	P_2O_5 - WS	%	2.8	(23%)
	K_2O	%	18.8	
	Mg	%	1.5	
	B	%	750	
	pH		4.8	
	Physical properties			
	Granule strenght	N	40	
	Abrasion	%	0.1	
	Volume weight	kg/l	0.82	
	Flowability	kg/min	5.4	
	CRH	%	23	
	Moisture absorption			
	80% RH			
	2 h	%	3.2	
	4 h	%	5.5	
	6 h		8.0	

Example 5

Bench scale process for solid granulation

GRADE	**12-6-24**
	kg/t
Urea (crushed)	264
SSP (P_2O_5 20%)	100
Morocco phosphate	130
KCl (white)	400
Colemanite	6
Bentonite	80

The mixture of solid raw materials and recycle was preheated to about 100 °C in the feeding screw of the granulator. Melting happened with hot air at the granulation drum. Granulation has been carried out at the granulator and partly at the cooling drum.

The products were coated with SK Fert FW5 AG 2 kg/t + talc 3 kg/t.

Very good or good granulation was obtained with a good product quality. The process conditions and results of product tests are shown in Table 5.

Table 5

	GRADE		**12-6-24**
	Feed + recycle kg/h		5.1
	Recycle ratio		0.84
	Granulation temperature °C		About 120
	Air from cooler	"	28
	Granulation		Very good
	Product properties		
	Chemical analyses		
	Water (KF)	%	0.27
	Urea - N	%	13.1
	P_2O_5 - Total	%	6.0
	P_2O_5 - NAC	%	2.9 (48%)
	P_2O_5 - WS	%	0.84 (14%)
	K_2O	%	25.8
	B	%	850
	pH		6.1
	Physical properties		
	Granule strenght	N	39
	Abrasion	%	0.1
	Volume weight	kg/l	0.84
	Flowability	kg/min	5.6
	CRH	%	15
	Moisture absorption		
	80% RH		
	2 h	%	2.1
	4 h	%	4.1
	6 h		6.0

Example 6

	GRADE 15-15-15
Urea (crushed)	285 kg/t
Urea melted	100 %
DAP	117 kg/t
Yunnan rock phosphate	330 kg/t
MOP	255 kg/t
Bentonite	6 kg/t

Urea was melted in a separate reactor and mixed with the other raw materials preheated to 90 °C. The temperature at the beginning of the granulation was 110.4 °C and at the end of the granulation 103.2 °C. The duration of the granulation stage was 4 minutes.

Product properties:

H_2O (KF)	0.09
Granule strenght N	34.5

Very good granulation was obtained.

Example 7

Bench scale process for solid granulation

	GRADE 15-15-15
Urea (46 %)	276 kg/t
DAP (17-45)	142 kg/t
Rock phosphate (P_2O_5 32 %)	270 kg/t
K_2SO_4 (K_2O 50 %)	300 kg/t

The mixture of solid raw materials and recycle was preheated to about 100 °C with IR in the feeding screw of the drum. The outer wall of the granulation drum was

heated with IR too. Urea was crushed beforehand. Small amount of hot air was used in the melting of urea in the granulation drum. Drying drum worked as cooler.

The products were coated with SK Fert FW5 AG 2 kg/t + talc 3 kg/t.

Process conditions:

Feed and recycle kg/h		5.07
Recycle ratio		0.75
Recycle heater °C		179
Granulation drum		
x Outside	°C	268
x Inside	"	117
Air to the drum	"	287
Air to cooler	"	24
Air from cooler	"	28
Granulation		Good

Product properties:

H_2O (KF)	%	0.09
N	"	15.5
P_2O_5 total	"	15.4
K_2O	"	16.1
S	"	6.6
Granule strenght N		30
Abrasion %		0.4
Shattering %		28
CRH %		18
Moisture abs.		
80 % RH		
2 h %		2.6
4 h %		4.8
6 h %		6.6

SOP based 15-15-15 granulated good.

Claims

1. A process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of:
providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material,
feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state,
feeding the molten or partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and
cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution,
provided that no water or aqueous liquid is introduced into the process.

2. A process according to claim 1, wherein the process is carried out continuously, and the molten portion of the feed material is kept constant during the process by controlling the flow rate of the feed material and the temperature of the melter.

3. A process according to claim 1 or 2, wherein the temperature of the molten or partly molten feed material is between 70 °C and 135 °C.

4. A process according to any of claims 1-3, wherein the melting is effected by introducing hot air into said melter.

5. A process according to claim 4, wherein the temperature of the hot air introduced into the melter is between 200 °C and 550 °C.

6. A process according to any of claims 1-5, wherein from 10 to 40% by weight of the feed material melts in the melter.

7. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises all individual components of the raw materials.

8. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises one or some of the individual components of the raw materials, and the rest of the components is fed to the granulator.

9. A process according to any of claims 1-8, wherein said solid feed material to be fed into the melter is preheated.

10. A process according to any of claims 1-9, wherein the solid raw material to be fed to the granulator is preheated.

11. A process according to claim 9 or 10, wherein the material is preheated to a temperature in the range from 80 °C to 110 °C.

12. A process according to any of claims 1-11, wherein the granulation temperature is in the range from 75 °C to 125 °C, preferably from 80 °C to 125 °C.

13. A process according to any of claims 1-12, wherein the fertilizer raw materials are selected from the group consisting of urea, diammonium phosphate (DAP), K_2SO_4 (SOP), monoammonium phosphate (MAP), potassium chloride (MOP), phosphate rock, single superphosphate (SSP), triple superphosphate (TSP), ammonium sulfate (AS) and ammonium chloride (AC).

14. A process according to claim 13, wherein the fertilizer raw materials comprise urea and at least one other of said fertilizer raw materials.

15. A process according to any of claims 1-14, wherein additionally at least one material selected from the group consisting of magnesium sulfate and micronutrients is introduced into the process.

16. A process according to any of claims 1-15, wherein additionally at least one filler selected from the group consisting of bentonite, calcite, calcium oxide, anhydrous calcium sulfate, calcium sulfate hemihydrate, dolomite, and sand, is introduced into the process.

17. A process according to claim 1, wherein the undersize material and the oversize material obtained in the screening are recirculated as said recycle material, said oversize material optionally being milled after the screening.

18. A process according to any of claims 1-17, wherein the moisture content of the dry compound fertilizer granules is below 0.6% by weight, preferably below 0.3% by weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 99/00568

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C05G 5/00, C05B 19/00, C05C 3/00, C05C 9/00, C05D 1/02, B01J 2/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C05B, C05C, C05D, C05G, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL, EDOC, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4008064 A (ÖYVIND SKAULI), 15 February 1977 (15.02.77), column 1, line 1 - line 12; column 2, line 13 - column 3, line 35; column 4, line 27 - column 8, line 22, figure 1, claims 1, 4-6, abstract --	1-18
X	GB 1462633 B (FISONS LIMITED), 26 January 1977 (26.01.77), page 1, line 21 - page 2, line 82, claim 4 --	1-18

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 1999	18 -10- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Ingrid Grundfelt/MP Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.. PCT/FI 99/00568

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 55015655 A (HITACHI METALS LTD) 1980-02-02 (abstract) World Patents Index (online). London U.K.: Derwent Publications, Ltd. (retrieved on 1999-10-04). Retrieved from: EPO WPI Database. DW 8011, Accession No 80-19312C & JP 55015655 (HITACHI METALS LTD) 1980-02-02 (abstract) (online) (retrieved on 1999-10-04) Retrieved from: EPO PAJ Database.	4
A	US 4398936 A (JOHAN W. HOOGENDONK ET AL), 16 August 1983 (16.08.83), column 1, line 33 - line 47; column 1, line 66 - column 2, line 5; column 2, line 39 - column 3, line 62, column 4, line 34 - line 40	1,8,10,13
A	JP 60065785 A DAIYA CHEMICAL KK et al 1985-04-15 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 1999-10-04). Retrieved from: EPO WPI Database. DW 198521. Accession No. 1985-126615.	1,15
A	US 5676729 A (JIM L. ELROD ET AL), 14 October 1997 (14.10.97), column 2, line 16 - line 21; column 3, line 15 - column 4, line 27, claim 1	1,13,16
A	US 4410350 A (GEORGE G. JUDD), 18 October 1983 (18.10.83), column 1, line 11 - line 36; column 2, line 66 - column 3, line 15, claim 1, abstract	1,13,14,16
A	WO 9629287 A1 (DEAD SEA WORKS LTD.), 26 Sept 1996 (26.09.96), page 2, line 11 - page 3, line 12; page 4, line 22 - page 8, line 18, figures 1,2	1-18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 99/00568

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1159445 B (PRODUITS CHIMIQUES PECHINEY-SAINT-GOBAIN), 23 July 1969 (23.07.69), page 1, line 43 - page 2, line 44; page 2, line 109 - page 4, line 26, claims 1-7,14,15	1-18

--

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/08/99

International application No.
PCT/FI 99/00568

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4008064 A	15/02/77	AU 8335975 A	27/01/77
		BE 831779 A	17/11/75
		BG 39806 A	15/08/86
		BR 7504741 A	06/07/76
		CA 1063778 A	09/10/79
		DD 118995 A	05/04/76
		DE 2533328 A,C	12/02/76
		DK 137068 B,C	16/01/78
		DK 338275 A	27/01/76
		EG 11720 A	29/03/78
		FI 62628 B,C	29/10/82
		FI 752127 A	27/01/76
		FR 2279457 A,B	20/02/76
		GB 1490003 A	26/10/77
		IE 41302 B	05/12/79
		IN 142375 A	02/07/77
		IT 1040154 B	20/12/79
		JP 1115790 C	29/09/82
		JP 51037098 A	29/03/76
		JP 56048202 B	14/11/81
		KE 2852 A	04/08/78
		NL 184097 B,C	16/11/88
		NL 7508914 A	28/01/76
		OA 5060 A	31/12/80
		RO 71993 A	30/06/81
		SE 395617 B,C	22/08/77
		SE 7508183 A	28/01/76
		TR 18469 A	24/02/77
		YU 40444 B	28/02/86
		YU 188775 A	28/02/82
GB 1462633 B	26/01/77	NONE	
US 4398936 A	16/08/83	AT 535 T	15/01/82
		BR 7904199 A	18/03/80
		CA 1120282 A	23/03/82
		EG 14816 A	30/06/85
		EP 0007132 A,B	23/01/80
		SE 0007132 T3	
		GR 72920 A	11/01/84
		IE 48161 B	17/10/84
		IN 152174 A	05/11/83
		JP 55010494 A	24/01/80
		JP 61009277 B	20/03/86
		NL 7807219 A	08/01/80
		SU 1056896 A	23/11/83
		TR 20420 A	26/06/81
		YU 40566 B	28/02/86
		YU 147679 A	21/01/83
US 5676729 A	14/10/97	AU 697843 B	15/10/98
		AU 6184296 A	30/01/97
		EP 0835232 A	15/04/98
		WO 9701518 A	16/01/97
US 4410350 A	18/10/83	NONE	

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/08/99

International application No.
PCT/FI 99/00568

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9629287 A1	26/09/96	AU 5146696 A	08/10/96
		CA 2213738 A	26/09/96
		IL 113104 A	26/01/99
GB 1159445 B	23/07/69	BE 699808 A	12/12/67
		DE 1592734 A	10/02/72
		DK 130632 B,C	17/03/75
		ES 341700 A	01/07/68
		NL 6708178 A	14/12/67

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C05G 5/00, C05B 19/00, C05C 3/00, 9/00, C05D 1/02, B01J 2/00

A1

(11) International Publication Number: **WO 00/00452**

(43) International Publication Date: 6 January 2000 (06.01.00)

(21) International Application Number: PCT/FI99/00568

(22) International Filing Date: 28 June 1999 (28.06.99)

(30) Priority Data:

981490	29 June 1998 (29.06.98)	FI
982013	18 September 1998 (18.09.98)	FI

(71) Applicant *(for all designated States except US)*: KEMIRA AGRO OY [FI/FI]; Porkkalankatu 3, FIN–00180 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: VAN BREMPT, Arthur [BE/BE]; Daalstraat 111, B–1852 Grimbergen (BE). POUKARI, Juhani [FI/FI]; Tinankuja 4 D 24, FIN–12430 Masala (FI).

(74) Agent: BERGGREN OY AB; P.O. Box 16, FIN–00101 Helsinki (FI).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: A PROCESS FOR THE PREPARATION OF COMPOUND FERTILIZER GRANULES

(57) Abstract

The invention relates to a process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of: providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material, feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state, feeding the molten or partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution, provided that no water or aqueous liquid is introduced into the process.

Claims

1. A process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of:
providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material,
feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state,
feeding the molten or partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and
cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution,
provided that no water or aqueous liquid is introduced into the process.

2. A process according to claim 1, wherein the process is carried out continuously, and the molten portion of the feed material is kept constant during the process by controlling the flow rate of the feed material and the temperature of the melter.

3. A process according to claim 1 or 2, wherein the temperature of the molten or partly molten feed material is between 70 °C and 135 °C.

4. A process according to any of claims 1-3, wherein the melting is effected by introducing hot air into said melter.

5. A process according to claim 4, wherein the temperature of the hot air introduced into the melter is between 200 °C and 550 °C.

6. A process according to any of claims 1-5, wherein from 10 to 40% by weight of the feed material melts in the melter.

7. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises all individual components of the raw materials.

8. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises one or some of the individual components of the raw materials, and the rest of the components is fed to the granulator.

A process for the preparation of compound fertilizer granules

The present invention relates to a process for the preparation of compound fertilizer granules by using solid granulation.

The term "compound fertilizer" is defined and used with several different meanings; it contains at least two of the plant nutrients nitrogen, phosphorus, and potassium. Compound fertilizers are produced chemically or by blending. They shall be in the form of granules, pellets, prills, or crystals and shall be free-flowing.

Compound fertilizers are manufactured and frequently used because they are convenient to produce, transport, store and apply and because they fulfil local or regional nutrient requirements, especially basal nutrient needs well. In addition to containing various ratios of the primary nutrients ($N + P_2O_5 + K_2$), the compound fertilizers may contain certain secondary and micronutrients specific to the crop needs in particular agroclimatic regions.

Granulated fertilizers have several advantages over powders, particularly in decreasing the quantity of dust, improving uniformity of flow when fertilizers are applied and segregation when they are blended.

In classifying the granulation methods, the physical properties of the materials to be granulated will be used. According to the density of the materials the following three groups may be distinguished: granulation of solids, granulation of slurries or of melts and granulation of fluids simultaneously with the reaction by which the product is formed.

Basic processes for manufacturing compound fertilizers are: Steam/water granulation, Chemical granulation or complex or slurry granulation, Drop forming or prilling, Compaction granulation and Dry mixing or blending.

The principal mechanisms responsible for initial fertilizer granule formation and subsequent growth are agglomeration and accretion. The known and widely applied compound fertilizer granulation methods are well reported for example in "Fertilizer Manual", Kluwer Academic Publishers, 1998, p. 434-451 and "Studies of Granulation of Compound Fertilizers Containing Urea: A Literature Review", G.C. Hicks, National Fertilizer Development Center; Bull Y-108, 15 pp., 1976.

Drop formation or prilling, compaction granulation, dry mixing or blending, etc. are also applied quite widely to produce different granular fertilizer formulations.

Because some water or moisture is always present in most traditional granulation processes, drying is an obligatory, difficult and expensive stage of the processes and cause the need of a separate dryer construction. To solve problems of granulation, product quality and drying different fertilizer grade-dependent processes are development.

A granulation process is described by Doshi, S.R. in the article "Fusion blend", Fertilizer Research vol. 30(1): p.87-97, 1991. Water (or steam) has been used to agglomerate solids either in powder, prilled or granulated form but no other liquids such as ammonia, phosphoric acid, or nitric acid are involved in the described process; still drying is essential.

Some water or moisture is always included in the process. The process is temperature and material moisture-related. For example, for the most agglomeration-type NPK fertilizers a liquid phase of about 300 kg/t of product is shown to be optimal.

Patent publication GB 1,189,398 (Sumitomo) discloses a process for producing a NK fertilizer which process comprises spraying a liquid mixture of urea, potassium chloride, gypsum and 1-10% by weight of water onto the solid material in a granulator. No drying is used. However, the amount of water added into the process is high enough to keep urea in dissolved state and the final product has a quite great water content of 1-2% by weight.

Patent publication US 4,138,750 (TVA) discloses a process for the production of fertilizers from phosphoric acid, sulfuric acid, anhydrous ammonia and urea where a specially designed pipe-cross reactor is used to produce a homogenous melt or slurry of low moisture content from phosphoric acid, sulfuric acid and anhydrous ammonia. The pipe-cross reactor eliminates the need for a preneutralizer and in addition, because of the low melt or slurry moisture content, the dryer is eliminated. The neutralization reaction heat is drying the material in the pipe-cross reactor.

Because of the water/moisture content of the raw materials and products, process and product quality problems, like increased hygroscopicity and plasticity, will often occur when fertilizers are granulated by using steam/water and chemical granulation processes; particularly when, for example SSP, TSP and/or urea is present in the product. The hygroscopicity and plasticity complicate drying,

According to a preferred embodiment of the invention the process is carried out continuously, and the molten portion of the feed material is kept constant during the process by controlling the flow rate of the feed material and the temperature of the hot air introduced into the melter. The optimal proportion of the molten feed material is dependent on the grade of the fertilizer wanted and the raw materials used. The optimal proportion of the molten material can for example be about 10-40 wt-%, preferably about 10-25 wt-%, more preferably about 12-20 wt-%, depending on the grade.

When melting is carried out by the aid of hot air a suitable temperature of the hot air introduced into the melter is between 200 and 550 °C. At the melter outlet the hot air has a temperature of about 90 °C to 120 °C.

Suitably the temperature of the molten or partly molten feed material leaving the melter is between 70 °C and 135 °C, preferably between 70 °C and 110 °C.

The process of the invention can be carried out either by introducing all individual components of the raw materials into the melter or by introducing one or some of the individual components of the raw materials into the melter and the rest of the components into the granulator.

The material to be fed into the melter and/or granulator can be preheated. This is preferred in view of the temperatur control of the process. The material can suitably be preheated to a temperature in the range from about 80 °C to about 110 °C.

The granulation temperature can vary depending on the formula of the fertilizer. The granulation temperature is preferably between about 75 °C and about 125 °C, more preferably between about 80 °C and about 125 °C.

The temperature of the cooled granulated product to be screened is typically between about 40 °C and 60 °C.

Typical solid fertilizer raw materials which can be used in the present invention are e.g. urea, diammonium phosphate (DAP), K_2SO_4 (SOP), monoammonium phosphate (MAP), phosphate rock, potassium chloride (MOP i.e. KCl), single superphosphate (SSP), triple superphosphate (TSP), ammonium sulfate (AS) and ammonium chloride (AC).

Preferably the fertilizer raw materials comprise urea, especially urea prills, and at least one other fertilizer raw material.

Example 1

Bench scale process for solid granulation.

Formulas (kg/t)

	GRADE		
Raw material	15-15-15 DAP+SSP	15-15-15 MAP+Sand	17-17-17 MAP+NH_4Cl
Urea	249	255	204
MAP(Lithuania 11-50)	-	300	340
DAP(Pernis 17-45)	210	-	-
SSP(Lithuania 19%)	287	-	-
NH_4Cl (N 26%)	-		153
KCl (K_2O 60%)	250	250	284
Sand	-	175	-

The mixture of the solid raw materials was fed to the bench scale granulator. Urea was added as prills. The melting of the mixture happened with hot air at the beginning of the granulator. Granulation was carried out at the granulator and partly at the cooler.

The process conditions and results are shown in Table 1.

Table 1

	GRADE		
	15-15-15 DAP+SSP	15-15-15 MAP+Sand	17-17-17 MAP+NH_4Cl
Process conditions:			
Feed + recycle kg/h	8.3	10.1	11.9
Recycle ratio	0.2	0.2	0.2
Air heater			
- temperature °C	336	316	322
- pressure bar	1.8	1.8	1.8
Temperature of product			
granulator outlet °C	97	92	97
cooler outlet	30	32	35
Granulation	Good	Very good	Good

Example 2

Bench scale process for solid granulation

GRADE	**NK 16-0-31**	
	2A	2B
Formula	16-0-31 Filler bentonite	16-0-31 Filler $CaSO_4$ hemihydrate
	kg/t	kg/t
Urea (prills)	348	348
KCl (white)	517	517
Bentonite	125	-
$CaSO_4*0.5H_2O$ (as dry matter)	-	125

The mixture of solid raw materials was fed with the recycle to the bench scale granulator. Melting happened with hot air at the beginning of the granulator. Granulation has been carried out at the granulator and partly at the cooler.

The products were coated with Esso coating oil 2 kg/t + talc 3 kg/t.

Very good or good granulation was obtained with a good product quality. However, the great humidity of air during the process caused some immediate increase of the water content of the final product.

The process conditions and results of the product tests are shown in Table 2.

Example 3

Bench scale process for solid granulation

GRADE	**18-12-6+1.5MgO**
	kg/t
Urea (prills)	172
KCl (white)	100
Kovdor phosphate	155
DAP (Pernis) 17-45	143
AS (Leuna)	366
$MgSO_4$	53

The mixture of solid raw materials was fed with the recycle to the bench scale granulator. Melting happened with hot air at the beginning of the granulator. Granulation has been carried out at the granulator and partly at the cooler.

The products were coated with Esso coating oil 2 kg/t + talc 3 kg/t.

Very good granulation was obtained with a good product quality. The process conditions and results of product tests are shown in Table 3.

Example 4

Bench scale process for solid granulation

GRADE	**12-12-17+2 MgO + 0.5 B_2O_3**
	kg/t
Urea (crushed)	264
Morocco phosphate	270
TSP (P_2O_5 45%)	89
KCl (white)	284
$MgSO_4$	64
Colemanite	6

The mixture of solid raw materials and recycle was preheated to about 100 °C in the feeding screw of the granulator. Melting happened with hot air at the granulation drum. Granulation has been carried out at the granulator and partly at the cooling drum.

The products were coated with SK Fert FW5 AG 2 kg/t + talc 3 kg/t.

Very good or good granulation was obtained with a good product quality. The process conditions and results of product tests are shown in Table 4.

Example 5

Bench scale process for solid granulation

GRADE	**12-6-24**
	kg/t
Urea (crushed)	264
SSP (P_2O_5 20%)	100
Morocco phosphate	130
KCl (white)	400
Colemanite	6
Bentonite	80

The mixture of solid raw materials and recycle was preheated to about 100 °C in the feeding screw of the granulator. Melting happened with hot air at the granulation drum. Granulation has been carried out at the granulator and partly at the cooling drum.

The products were coated with SK Fert FW5 AG 2 kg/t + talc 3 kg/t.

Very good or good granulation was obtained with a good product quality. The process conditions and results of product tests are shown in Table 5.

Example 6

	GRADE 15-15-15
Urea (crushed)	285 kg/t
Urea melted	100 %
DAP	117 kg/t
Yunnan rock phosphate	330 kg/t
MOP	255 kg/t
Bentonite	6 kg/t

Urea was melted in a separate reactor and mixed with the other raw materials preheated to 90 °C. The temperature at the beginning of the granulation was 110.4 °C and at the end of the granulation 103.2 °C. The duration of the granulation stage was 4 minutes.

Product properties:

H_2O (KF)	0.09
Granule strenght N	34.5

Very good granulation was obtained.

Example 7

Bench scale process for solid granulation

	GRADE 15-15-15
Urea (46 %)	276 kg/t
DAP (17-45)	142 kg/t
Rock phosphate (P_2O_5 32 %)	270 kg/t
K_2SO_4 (K_2O 50 %)	300 kg/t

The mixture of solid raw materials and recycle was preheated to about 100 °C with IR in the feeding screw of the drum. The outer wall of the granulation drum was

Claims

1. A process for the preparation of compound fertilizer granules containing at least two of the plant nutrients nitrogen, phosphorus and potassium, said process comprising the steps of:
providing a solid feed material comprising at least one solid fertilizer raw material and optionally recycle material,
feeding the feed material or a part thereof into a melter for melting a desired portion thereof and keeping said portion in molten state,
feeding the molten or partly molten material and optionally other desired solid raw materials to a granulator to obtain a granulated product, and
cooling and optionally screening the granulated product to obtain dry compound fertilizer granules having a desired size distribution,
provided that no water or aqueous liquid is introduced into the process.

2. A process according to claim 1, wherein the process is carried out continuously, and the molten portion of the feed material is kept constant during the process by controlling the flow rate of the feed material and the temperature of the melter.

3. A process according to claim 1 or 2, wherein the temperature of the molten or partly molten feed material is between 70 °C and 135 °C.

4. A process according to any of claims 1-3, wherein the melting is effected by introducing hot air into said melter.

5. A process according to claim 4, wherein the temperature of the hot air introduced into the melter is between 200 °C and 550 °C.

6. A process according to any of claims 1-5, wherein from 10 to 40% by weight of the feed material melts in the melter.

7. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises all individual components of the raw materials.

8. A process according to any of claims 1-6, wherein said solid feed material to be fed into the melter comprises one or some of the individual components of the raw materials, and the rest of the components is fed to the granulator.

DERWENT-ACC-NO: 1975-06732W
DERWENT-WEEK: 197504

TITLE: Granulating a composite fertiliser mixt. - by rapidly homogenising the molten slurry and solidifying droplets in a tower with air flow
PATENT-ASSIGNEE: MITSUI TOATSU CHEM INC[MITK]
PRIORITY-DATA: 1969JP-0015027 (March 1, 1969)
PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 74049116 B	December 25, 1974	N/A	000	N/A

INT-CL (IPC): B01J002/04
ABSTRACTED-PUB-NO: JP74049116B
BASIC-ABSTRACT: A composite fertiliser in which the components are insol. on only partially soluble is mixed in the molten state by a pneumatic homogeniser revolving at 10,000-30,000 rev sec-1. The slurry is granulated by dropwise introduction to a hollow tower with a current of air. The prod is screened after cooling. The fertiliser may contain ammonium nitrate, urea potassium salts, phosphates, ammonium salts, and opt. herbicides and insecticides.
DERWENT-CLASS: C04
CPI-CODES: C05-A01A; C05-B02A4; C05-C01; C10-A13C; C11-C05; C12-N09;

---------- KWIC ---------

Title - TIX:

Granulating a composite fertiliser mixt. - by rapidly homogenising the molten slurry and solidifying droplets in a tower with air flow

Basic Abstract Text - ABTX:

A composite fertiliser in which the components are insol. on only partially soluble is mixed in the molten state by a pneumatic homogeniser revolving at 10,000-30,000 rev sec-1. The slurry is granulated by dropwise introduction to a hollow tower with a current of air. The prod is screened after cooling. The fertiliser may contain ammonium nitrate, urea potassium salts, phosphates, ammonium salts, and opt. herbicides and insecticides.

DERWENT-ACC-NO: 1975-42103W
DERWENT-WEEK: 197525

TITLE: Granulator for molten fertilizer, urea, etc. - with screw blades and
alternate upright and inverted cone coolers
PATENT-ASSIGNEE: DZERZ CHEM ENGG RES[DZCHR]
PRIORITY-DATA: 1970SU-1469124 (August 6, 1970)
PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
SU 405238 A	January 29, 1975	N/A	000	N/A

INT-CL (IPC): B01J002/02
ABSTRACTED-PUB-NO: SU 405238A
BASIC-ABSTRACT: The screw is provided to reduce the height of the apparatus and
is mounted above the conical cooling screens on a shaft which rotates it in a
direction opposite to that in which the helix of the blades turn. Molten
fertilizer or urea arrives down is fed to the distributor. Finely-dispersed
powdered talkc is injected across the path from the spray heads in a flow of
dry air. The shaft with the blades rotates. The flow of molten material
coming through the perforations is distributed in the form of droplets, which
become covered in talc, eventually fall and are conveyed to the arrangement of
cones. Because of the arrangement of the screw and its rotation, the impact
with which the solidified granules strike its surface is reduced. The
increased speed with which the screw blade rotates ensures that the degree of
dampening of the impact is also increased. The finished granules have a
downward movment which is far less in a free fall, resulting in a lesser degree
of surface crystallization than known with conventional apparatus.
DERWENT-CLASS: C04 J04
CPI-CODES: C10-A13C; C11-C05; C12-M11; C12-N10; J04-A05;

---------- KWIC ---------

Title - TIX:

Granulator for molten fertilizer, urea, etc. - with screw blades and alternate
upright and inverted cone coolers

DERWENT-ACC-NO: 1979-77372B
DERWENT-WEEK: 197943

TITLE: Prodn. of ammonium nitrate and calcium carbonate mixt. - with concn. of
nitrate soln. before mixing to prevent corrosion
INVENTOR: MORARU, O; PANY, V ; POPOVICI, N
PATENT-ASSIGNEE: COMB AZOMURES INGRA[AZOMN]
PRIORITY-DATA: 1978DD-0205481 (May 19, 1978)
PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
DD 137093 A	August 15, 1979	N/A	000	N/A
CS 7802780 A	October 31, 1979	N/A	000	N/A
FR 2424877 A	January 4, 1980	N/A	000	N/A
JP 54153161 A	December 3, 1979	N/A	000	N/A
NO 7801468 A	November 19, 1979	N/A	000	N/A

INT-CL (IPC): C01C001/18; C01F011/06 ; C05C005/00
ABSTRACTED-PUB-NO: DD 137093A
BASIC-ABSTRACT: Prodn. of a mixt. of NH4NO3 and CaCo3 comprises mixing a
homogeneous melt of NH4NO3 soln., stabiliser and recycled fines with a reactive
form of CaCo3 which has been heated to 175 degrees C in a fluidised bed. The
compsn. is mixed for 3-30 sec at 175-180 degrees C, then granulated and sieved.
The CaCo3 used is waste material from prodn. of Na2Co3 or fertiliser. The melt
has been concentrated to 99.7% dry matter content and is melted at 175 degrees
C.

The prod. has improved quality and reduced Ca(NO2)2 content. By concn. of the
NH4NO3 soln. before reaction corrosion of feed lines, pumps and equipment is
prevented.
DERWENT-CLASS: C04 E33 E35
CPI-CODES: C05-A01B; C05-C01; C11-C05; E32-A; E34-D03;

---------- KWIC ---------

Basic Abstract Text - ABTX:

Prodn. of a mixt. of NH4NO3 and CaCo3 comprises mixing a homogeneous melt of
NH4NO3 soln., stabiliser and recycled fines with a reactive form of CaCo3 which
has been heated to 175 degrees C in a fluidised bed. The compsn. is mixed for
3-30 sec at 175-180 degrees C, then granulated and sieved. The CaCo3 used is
waste material from prodn. of Na2Co3 or fertiliser. The melt has been
concentrated to 99.7% dry matter content and is melted at 175 degrees C.

RÉPUBLIQUE FRANÇAISE

INSTITUT NATIONAL
DE LA PROPRIÉTÉ INDUSTRIELLE

PARIS

(11) N° de publication : **2 424 877**

(A n'utiliser que pour les commandes de reproduction).

A1

DEMANDE DE BREVET D'INVENTION

(21) N° **78 13158**

(54) **Procédé et installation pour la fabrication du nitrate de chaux ammoniacal.**

(51) Classification internationale (Int. Cl.²). **C 01 F 11/40.**

(22) Date de dépôt ..... 3 mai 1978, à 15 h 38 mn.

(33) (32) (31) Priorité revendiquée :

(41) Date de la mise à la disposition du public de la demande ..... B.O.P.I. — «Listes» n. 48 du 30-11-1979.

(71) Déposant : AZOMURES COMBINATUL DE INGRASAMINTE CHIMICE TIRGU-MURES, résidant en Roumanie.

(72) Invention de : Octavian Moraru, Venera Pany, Neculai Popovici, Constantin Pitis, Gheorgh Macaveiu et Vasile Anescu.

(73) Titulaire : *Idem* (71)

(74) Mandataire : Cabinet Malémont, 42, avenue du Président-Wilson, 75116 Paris.

D Vente des fascicules à l'IMPRIMERIE NATIONALE, 27, rue de la Convention — 75732 PARIS *CEDEX 15*

2424877

La présente invention a pour objet un procédé et une installation pour la fabrication du nitrate de chaux ammoniacal de qualité supérieure, à basse teneur en azotate de calcium.

On connaît déjà divers procédés de fabrication du nitrate de chaux ammoniacal qui consistent dans le mélange du calcaire ou de la dolomite avec une solution d'azotate d'ammonium, avant la concentration de cette dernière ; mais ces procédés présentent des inconvénients tels que la corrosion des conduits de inculation, des pompes et des appareils pour la concentration et l'obtention de nitrate de chaux ammoniacal à une teneur élevée en azotate de calcium qui affecte sa qualité.

Le procédé selon l'invention élimine ces inconvénients. En effet, afin d'éviter la corrosion des conduits, des pompes et des appareils, le mélange constitué par la solution d'azotate d'ammonium, l'agent stabilisant et le matériau rejeté au cours du tirage final du nitrate de chaux ammoniacal, obtenu après l'homogénéisation est concentré jusqu'à 99,7 % résidu sec, après quoi il est fondu à la température de 175°C et mélangé avec le carbonate de calcium réactif, sous-produit de fabrication de la soude et des engrais, préchauffé à 175°C en lit fluidisé. Le mélange a lieu pendant 3 à 30 secondes à une température comprise entre 175 et 180°C, après quoi le produit est granulé et tamisé.

Le procédé est mis en oeuvre dans une installation formée d'un récipient d'homogénéisation muni d'un agitateur et d'un système de chauffage, relié par l'intermédiaire de conduites et d'une pompe au concentrateur tubulaire relié à son tour à un récipient d'homogénéisation qui communique par sa partie supérieure (par l'intermédiaire d'une vis sans fin) avec un préchauffeur à lit fluidisé, à l'intérieur duquel est disposé un faisceau tubulaire, et par sa partie inférieure avec un tour de granulation.

On donne ci-après un exemple de réalisation de l'invention, conformément à la figure ci-jointe qui représente le schéma technologique de l'installation.

Dans le récipient d'homogénéisation 1, muni d'un agitateur 2 et d'un système de chauffage 3, on introduit la solution d'azotate d'ammonium, l'agent stabilisant comme par exemple le phosphate, le polyphosphate ou le sulfate d'ammonium à raison de 1 à 2 % par rapport à la quantité totale de mélange, et le matériau rejeté au cours du tirage final du nitrate de chaux ammoniacal. Après homogénéisation, le mélange est amené par la conduite 4, la pompe centrifuge 5 munie d'un chemisage de chauffage et la conduite 6, au système de concentrateur tubulaire 7 chauffé à la vapeur saturée de 14 atm amenée par la conduite 8.

La masse fondue obtenue dans ce concentrateur, d'une concentration de 99,7 % résidu sec, est envoyée par la conduite 9 dans le récipient d'homogénéisation 10, qui est muni d'un agitateur 11 et d'un système de chauffage 12 et dans lequel, par l'intermédiaire de la conduite 13 et la vis sans fin à doser 14,

est amené le carbonate de calcium préchauffé à 175°C dans un préchauffeur 15 à lit fluidisé.

Le préchauffeur 15 à lit fluidisé est formé d'une enveloppe 16 contenant dans sa partie intérieure un faisceau tubulaire 17 et d'une conduite 18 amenant le carbonate de calcium.

On utilise l'air chaud comme agent de chauffage et de fluidisation.

Dans le récipient d'homogénéisation 10 a lieu un mélange intense et intime de la masse fondue d'azotate d'ammonium avec le carbonate de calcium préchauffé dans un très court intervalle de temps de 3 à 30 secondes et à une température comprise entre 175° et 180°C. La masse fondue obtenue à la température de 175°C est transportée par la conduite 19 et est dispersée par le granulateur centrifuge 20 dans la tour en béton 21. Par refroidissement à l'aide d'un courant d'air provenant de la partie inférieure de la tour 21 et créé par la soufflante 22, il se forme des granules sphériques de nitrate de chaux ammoniacal, qui sont prélevées à la partie inférieure de la tour 21 à l'aide du transporteur 23 et envoyées par la conduite 24 vers les tamis 25 (qui tirent le produit grossier) et de là par la conduite 26 aux refroidisseurs 27 à lit fluidisé.

Après refroidissement de 100°C jusqu'à 28-30°C à l'air conditionné obtenu dans l'installation de conditionnement, le nitrate de chaux ammoniacal est transporté par la conduite 28 vers les tamis 29 de tirage après quoi, il est déversé par la conduite 30 dans les tambours de poudrage où il est poudré en vue d'empêcher le phénomène d'agglomération.

Après le poudrage, le nitrate de chaux ammoniacal est passé sur la bande peseuse 32 puis amené vers un dépôt de stockage.

Dans le procédé selon l'invention, on utilise un carbonate de calcium réactif (précipité) qui est un sous-produit dans l'industrie des engrais complexes NPK ou de la soude.

Grâce à la réactivité du carbonate de calcium utilisé et à la température élevée à laquelle on opère, la durée de contact dans le récipient d'homogénéisation est très courte ce qui conduit finalement à l'obtention d'un produit à basse teneur en azotate de calcium, composant qui affecte la qualité du nitrate de chaux ammoniacal.

L'invention présente donc l'avantage de permettre l'obtention d'un produit de qualité supérieure dans une installation simple et facile à réaliser.

REVENDICATIONS

1. Procédé d'obtention du nitrate de chaux ammoniacal, caractérisé en ce que dans le but d'éviter la corrosion des conduites, des pompes et des appareils, la solution d'azotate d'ammonium, l'agent stabilisant et le matériau rejeté au cours du tirage final du nitrate de chaux ammoniacal produit, sont concentrés après homogénéisation, jusqu'à environ 99,7 % résidu sec, puis fondus à la température de 175°C et ensuite mélangés avec le carbonate de calcium réactif, sous-produit de la fabrication de la soude et des engrais, préchauffé à 175°C en lit fluidisé, ce mélange ayant lieu pendant 3-30 secondes et à une température comprise entre 175 et 180°C, et cette opération de mélange étant munie d'une opération de granulation et de tirage.

2. Installation selon la revendication 1, caractérisée en ce qu'elle est formée d'un récipient d'homogénéisation (1) muni d'un agitateur (2) et d'un système de chauffage (3) relié par l'intermédiaire de conduites (4,6) et d'une pompe (5) d'un concentrateur tubulaire (7) lui même relié à un récipient d'homogénéisation (10) qui communique par sa partie supérieure, par l'intermédiaire d'une vis sans fin (14) avec un préchauffeur (16) à lit fluidisé à l'intérieur duquel est disposé un faisceau tubulaire (17) et, par sa partie inférieure avec une tour de granulation (21).

Pl. UNIQUE

2424877